Electrical properties

Frequency dependence

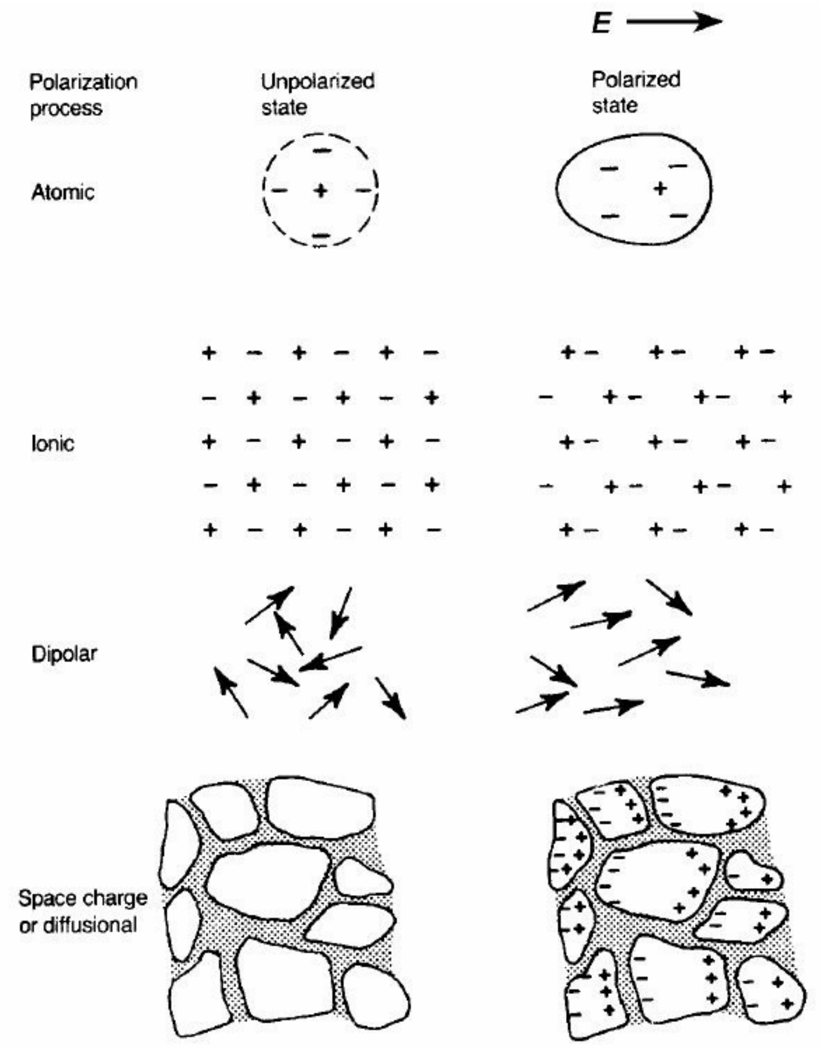
Impedance spectroscopy (IS)

-Electrical properties

- Dynamical behavior

- Dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material:
    - ionic
    - semiconducting
    - mixed electronic–ionic
    - insulators (dielectrics).

Electrical properties

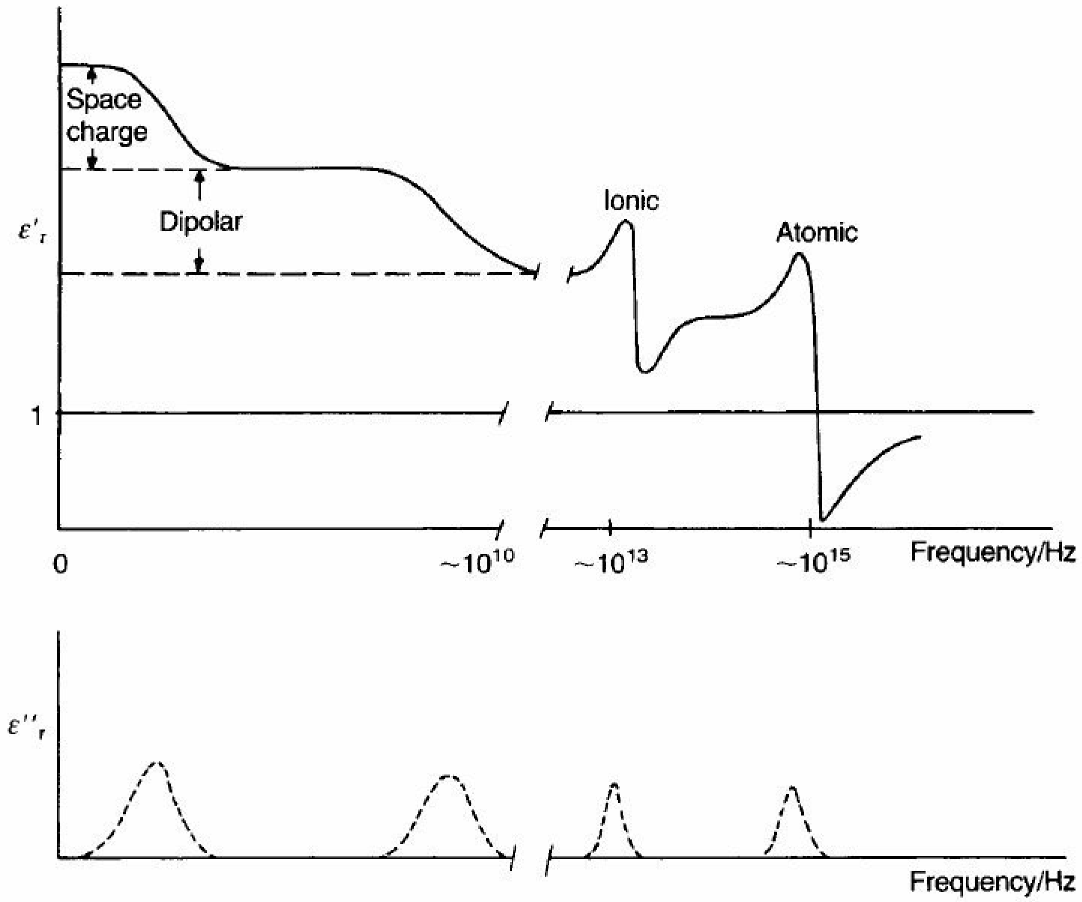


Various polarization processes.

Polarization mechanisms

Dynamics
Polarization relaxation

Electrical properties



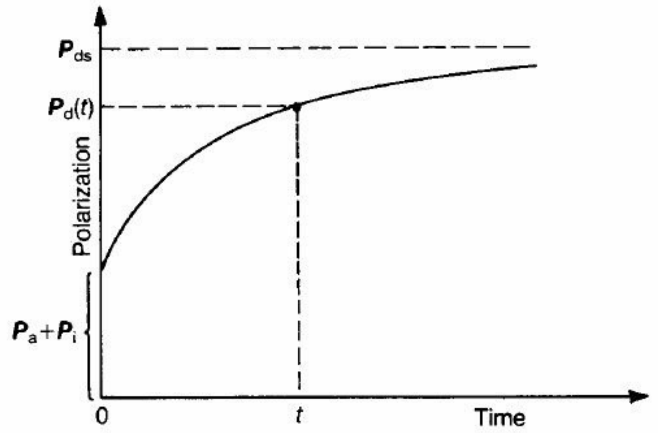
Variation of ε_r' and ε_r'' with frequency. Space charge and dipolar polarizations are relaxation processes and are strongly temperature dependent; ionic and electronic polarizations are resonance processes and sensibly temperature independent. Over critical frequency ranges energy dissipation is a maximum as shown by peaks in $\varepsilon_r''(\omega)$.

Electrical properties

DC Electric fields

$$\frac{dP_d}{dt} = \frac{1}{\tau}\left[P_{ds} - P_d(t)\right] \longrightarrow P_d(t) = P_{ds}\left(1 - e^{-\frac{t}{\tau}}\right)$$

τ -> relaxation time



Development of polarization by slow diffusional processes; P_a and P_i are the 'instantaneous' atomic and ionic polarization processes capable of responding to very high frequency (∞) fields.

Electrical properties

AC Electric fields $E = E_0\, e^{i\omega t}$

$$\frac{dP_d}{dt} = \frac{1}{\tau}\left[(\varepsilon(0) - \varepsilon(\infty))E - P_d(t)\right]$$

Dielectric permittivity

$$\varepsilon = \varepsilon(\infty) + \frac{\Delta\varepsilon}{1 + i\omega\tau}$$

Debye relaxation

$$\varepsilon = \varepsilon' - i\varepsilon''$$

$$\varepsilon' = \varepsilon(\infty) + \frac{\Delta\varepsilon}{1 + \omega^2\tau^2}$$

$$\varepsilon'' = \frac{\omega\tau\,\Delta\varepsilon}{1 + \omega^2\tau^2}$$

$$\tau = \tau_0\, e^{-\frac{E_A}{k_B T}}$$

E_A -> activation energy

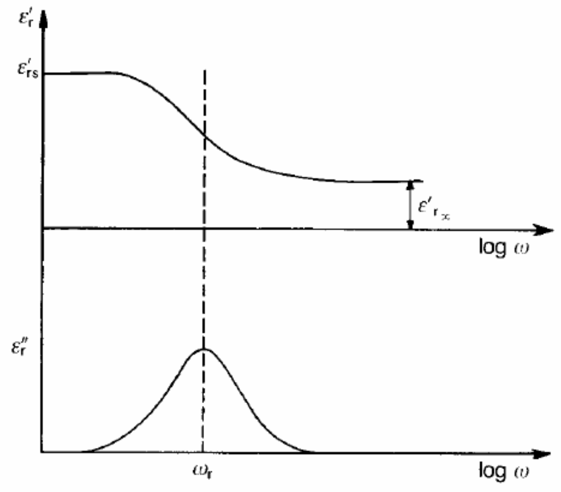
Distribution G(τ) of relaxation times

$$\varepsilon = \varepsilon(\infty) + (\varepsilon(0) - \varepsilon(\infty))\int_0^\infty \frac{G(\tau)}{1 + i\omega\tau}\, d\tau$$

Dielectric Relaxation in Materials with a Single Time Constant

$$P_d(t) = \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + i\omega\tau} E = \frac{\Delta\varepsilon}{1 + i\omega\tau} E$$

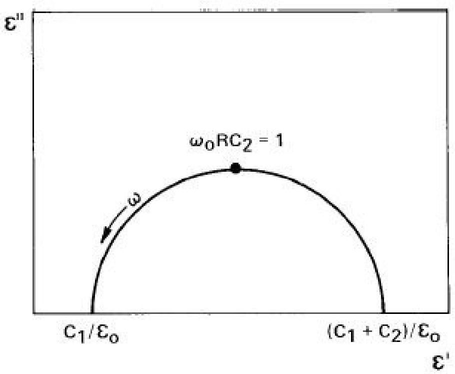
ε(0) -> static
ε(∞) -> high frequency
τ -> relaxation time



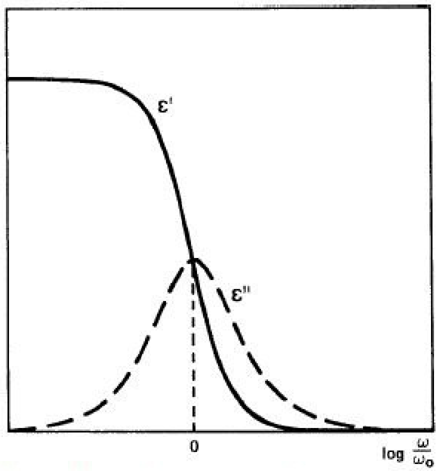
Variation in permittivity with frequency for a dielectric showing 'Debye' relaxation.

Electrical properties

Dielectric Relaxation in Materials with a Single Time Constant. Equivalent circuits



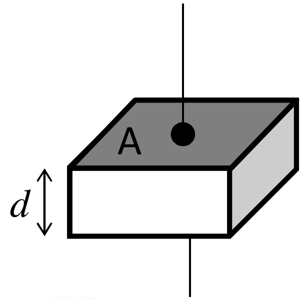
Complex plane plot of the frequency dependence of the complex permittivity modeled by the circuit of Figure

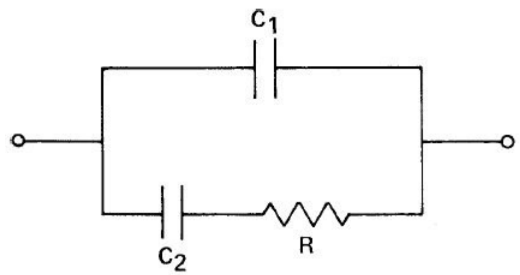


Real and imaginary parts of the complex permittivity as a function of normalized radial frequency.

Admittance (Z is the impedance):

$$Y = \frac{1}{Z} = i\omega C_0 \varepsilon \qquad C_0 = \varepsilon_0 \frac{A}{d}$$





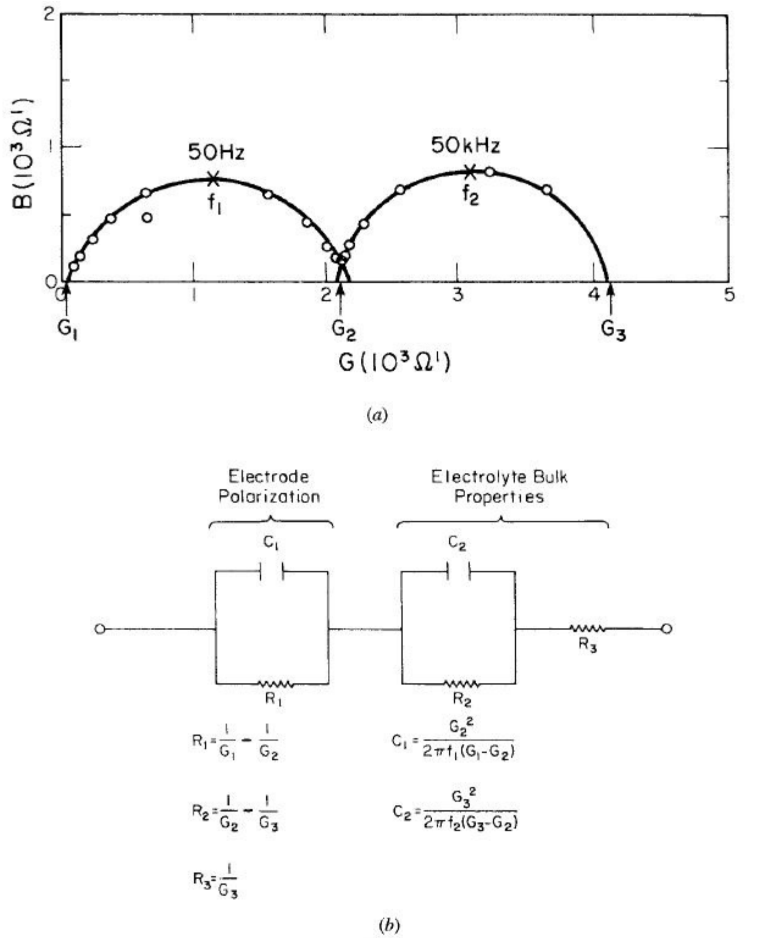
The Debye equivalent circuit.

$$Y = i\omega C_1 + \frac{\omega^2 R C_2^2}{1+\omega^2 R^2 C_2^2} + i\frac{\omega C_2}{1+\omega^2 R^2 C_2^2}$$

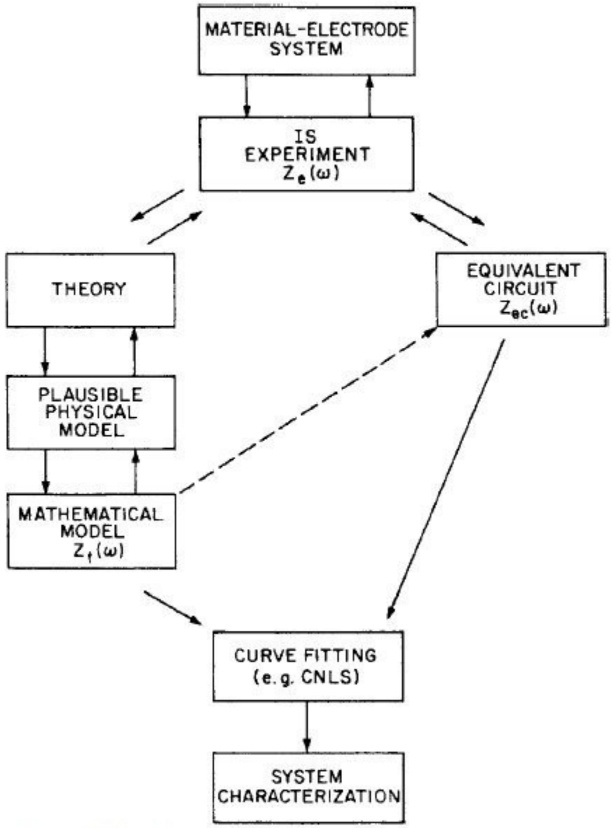
$$\varepsilon = \varepsilon(\infty) + \frac{\Delta\varepsilon}{1+\omega^2\tau^2} - i\frac{\omega\tau\,\Delta\varepsilon}{1+\omega^2\tau^2}$$

$$\tau = RC_2; \quad C_1 = \varepsilon(\infty)\,\varepsilon_0\frac{A}{d}; \quad C_2 = \Delta\varepsilon\,\varepsilon_0\frac{A}{d}$$

Electrical properties



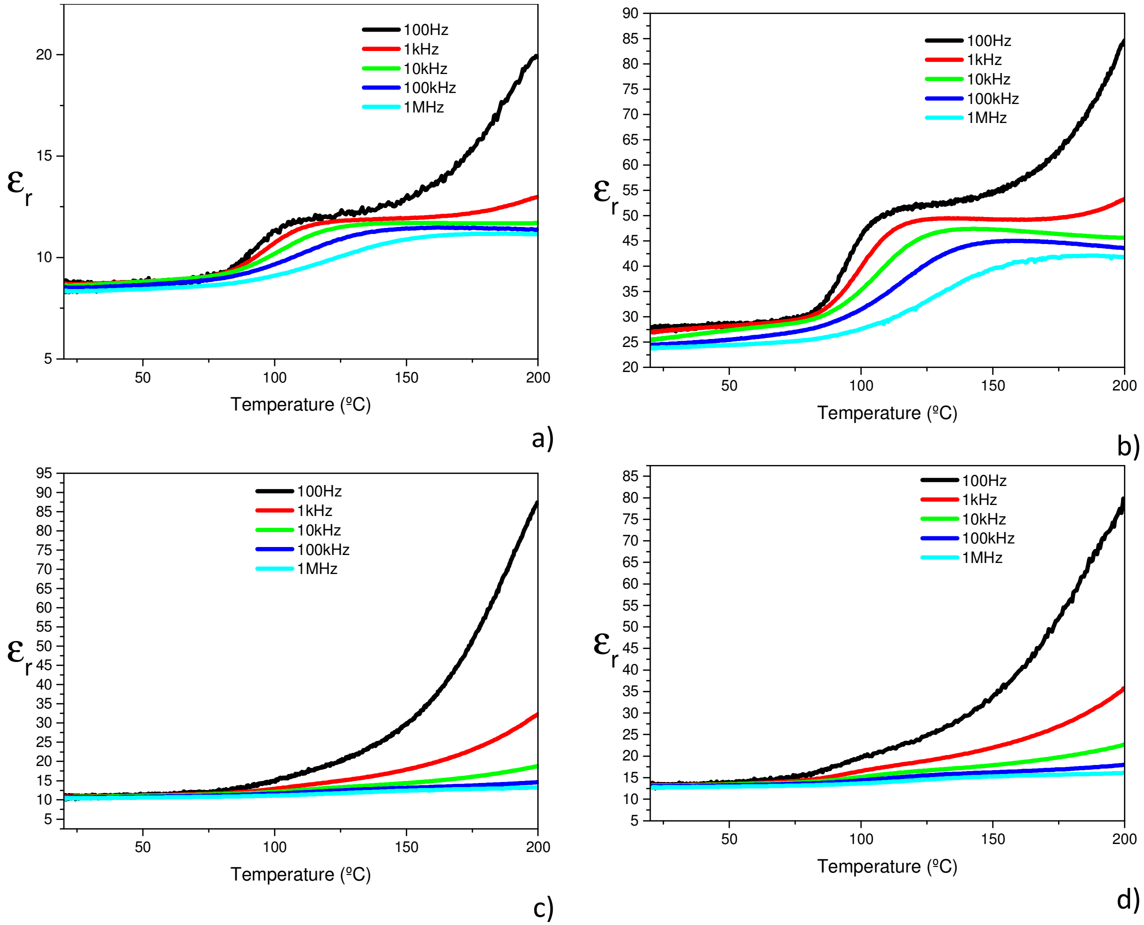
(*a*) Admittance behavior of the electrochemical cell given in TABLE1.4.4 at 873 K for a specimen with naturally porous electrodes (sputtered Pt). (*b*) The equivalent circuit for the behavior in part *a* showing the two impedance elements associated with each semicircle.



Flow diagram for the measurement and characterization of a material–electrode

Electrodes, grains *vs* grain boundaries, etc

Dielectric properties: Temperature dependence



Relative dielectric permitivity *vs* temperature:

- 0.2mbar of oxigen pressure;
- 80mJ/cm2 of laser annealing;
- a) 0 seconds, b) 50 seconds, c) 200 seconds and d) 1000 seconds.

Difuse phase transition

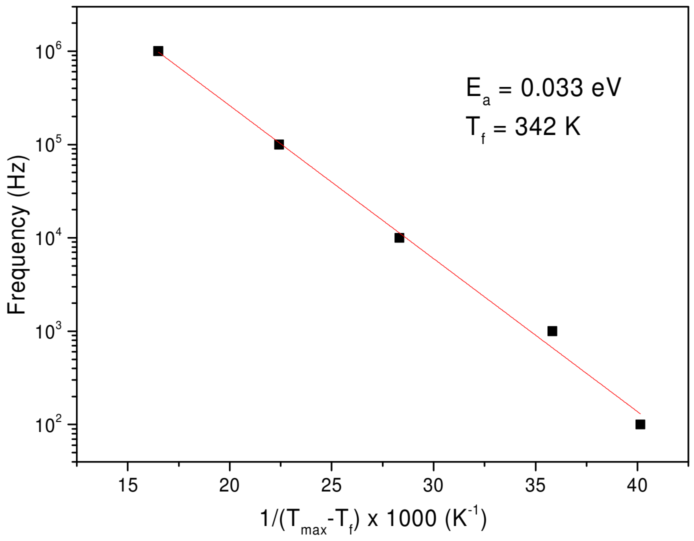
Transition temperature peaks depend on frequency (relaxor-like behaviour)

Dielectric properties

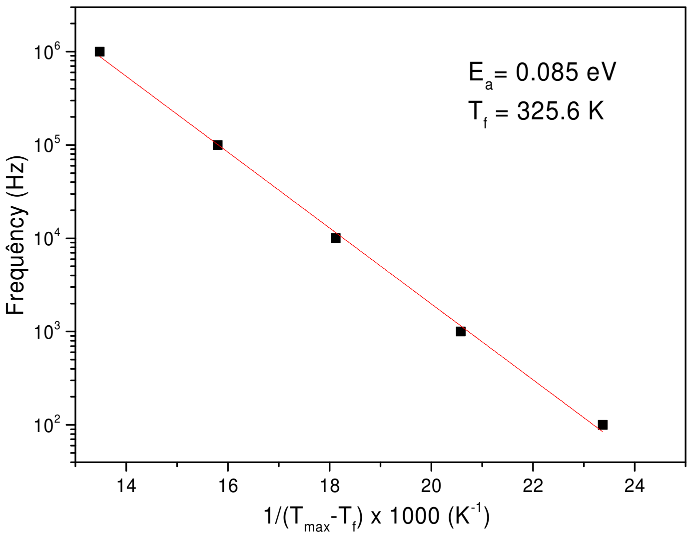
Vogel-Fulcher

$$f = f_0 \cdot \exp\left(-\frac{E_a}{k_B(T_{max} - T_f)}\right)$$

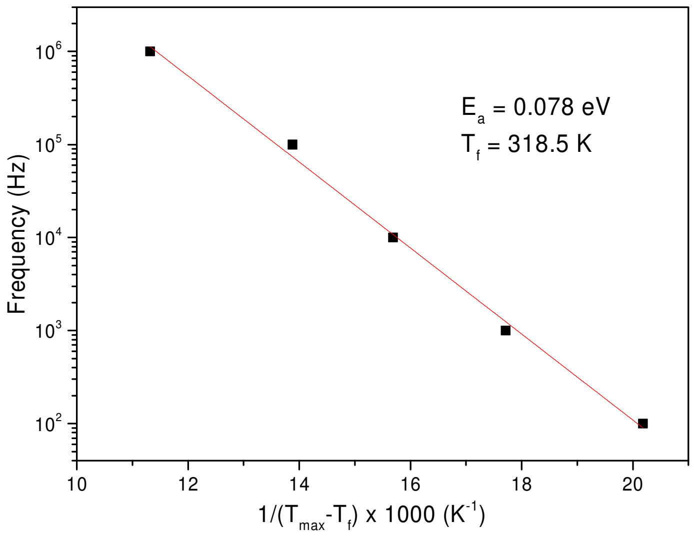
50 mJ/cm² - 1000 seconds



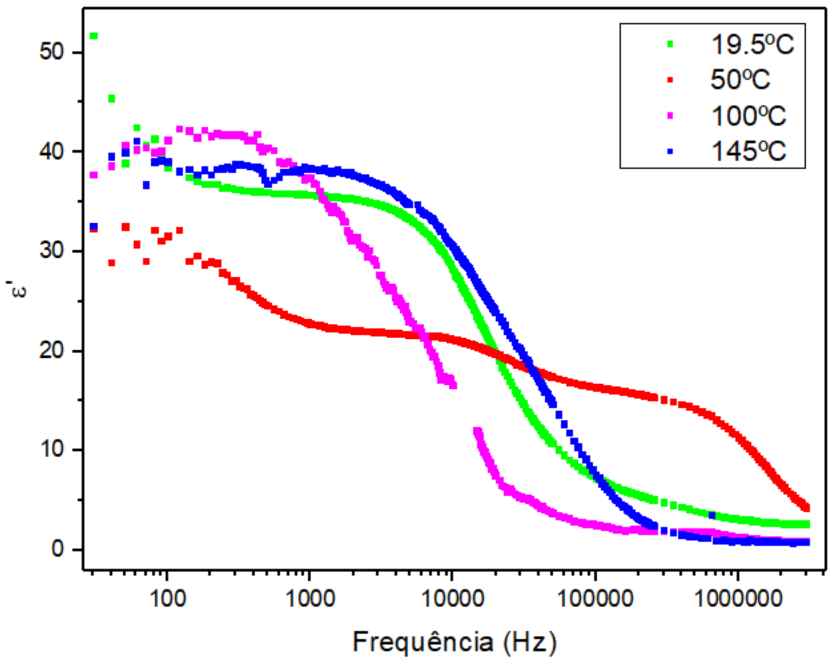
Without laser anealing



80 mJ/cm² - 50 seconds



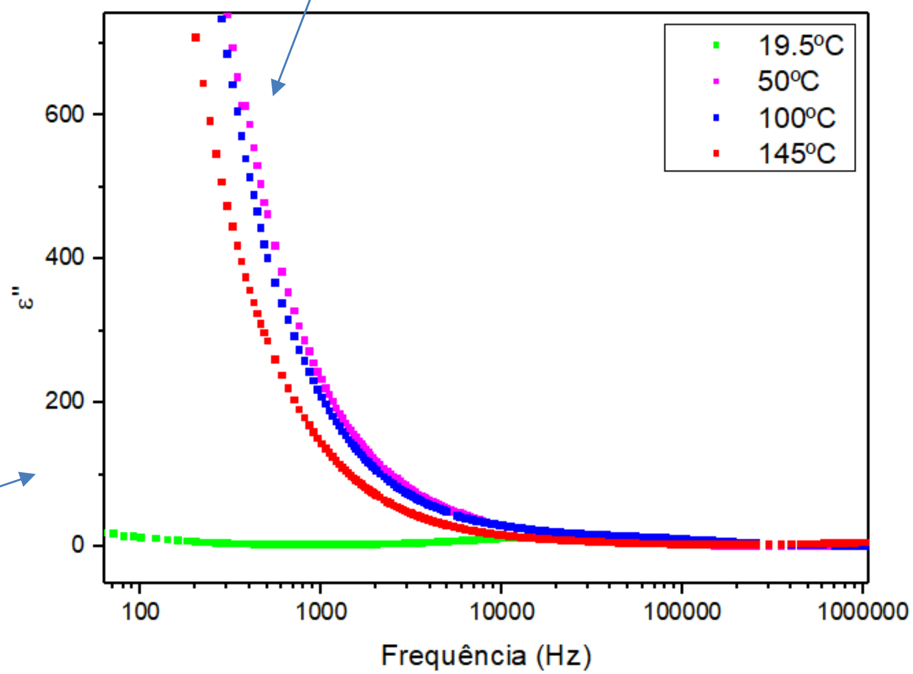
Dielectric properties: Frequency dependence



Real part of permittivity

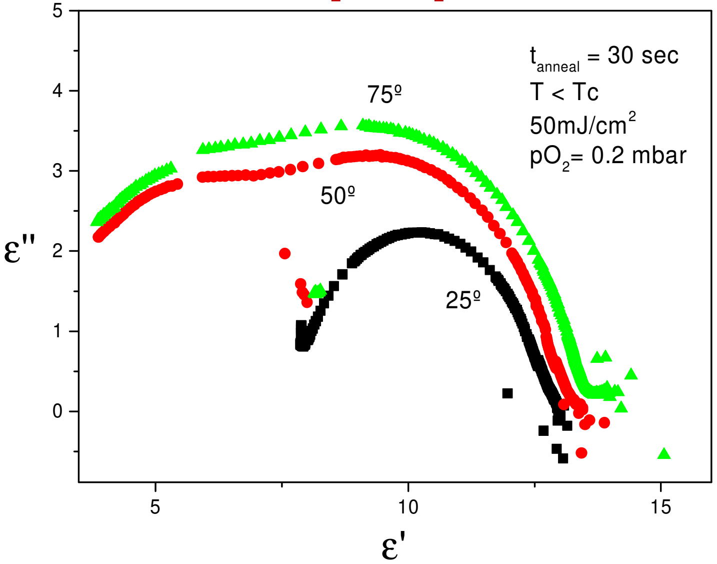
Srong rise at low temperatures: conductivity

$$\varepsilon = \frac{\sigma_{DC}}{\varepsilon_\infty \ \omega^s}$$



Imaginary part of permittivity

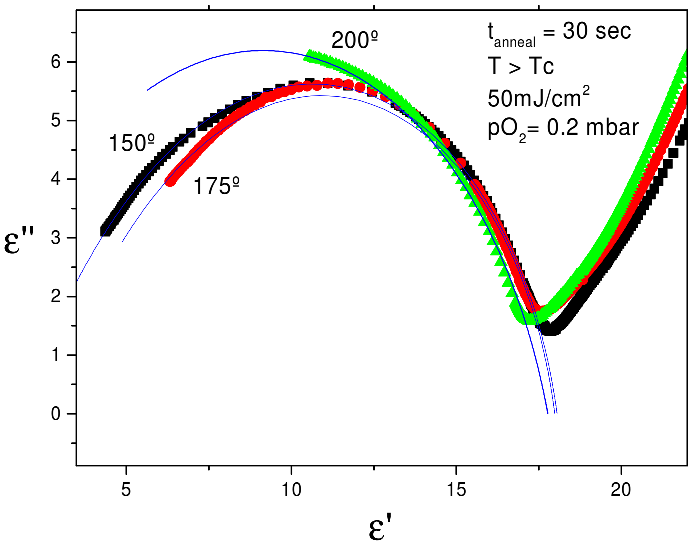
Dielectric properties



Lower fluence; Higher oxygen

Havriliak-Negami

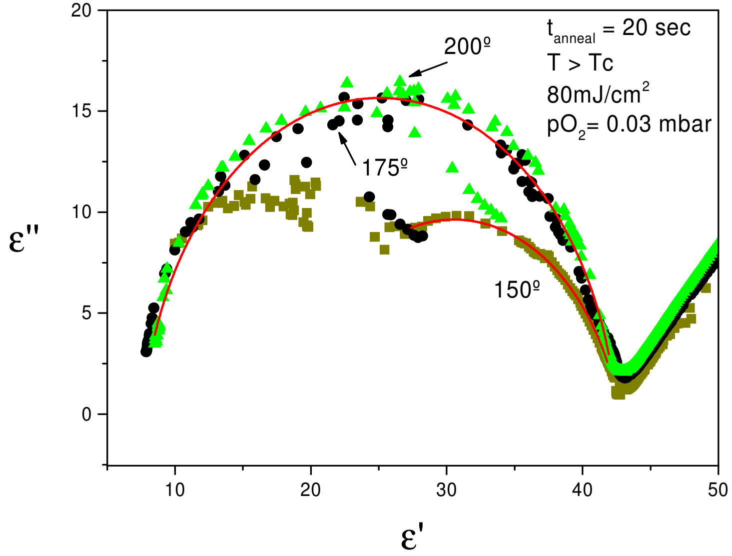
$$\varepsilon = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1+(i\omega\tau)^\alpha\right)^\beta}$$



Cole-Cole (β=1)

$$\varepsilon = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(i\omega\tau)^\alpha}$$

Higher fluence
Lower oxygen



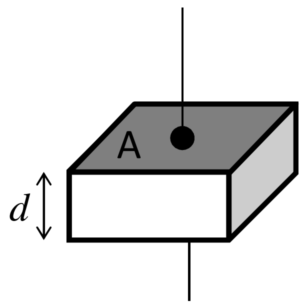
Electrical properties

Table 3.1. Compilation of different model functions for the frequency domain

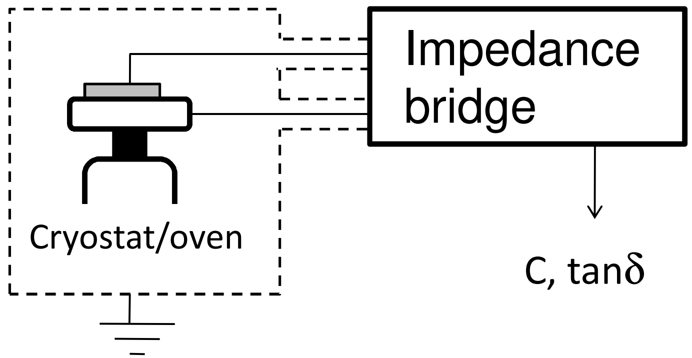
	Dielectric function	Real part	Imaginary part	Relaxation Time Distribution
Model function	$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\Delta\varepsilon}$	$\frac{\varepsilon'(\omega)-\varepsilon_\infty}{\Delta\varepsilon}$	$\frac{\varepsilon''(\omega)}{\Delta\varepsilon}$	$L(\tau)$
Debye	$\frac{1}{1+i\omega\tau_D}$	$\frac{1}{1+(\omega\tau_D)^2}$	$\frac{\omega\tau_D}{1+(\omega\tau_D)^2}$	$\delta(\tau_D)$
Cole/Cole	$\frac{1}{1+(i\omega\tau_{CC})^\beta}$ $0<\beta\le 1$	$(1+\omega\,\tau_{CC})^\beta\cos(\beta\,\pi/2))\,r^{-1}(\omega)$ $r(\omega)=1+2(\omega\tau_{CC})^\beta\cos(\beta\pi/2)+(\omega\tau_{CC})^{2\beta}$	$(\omega\,\tau_{CC})^\beta\sin(\beta\,\pi/2))\,r^{-1}(\omega)$	$\frac{1}{2\pi}\frac{\sin\beta\pi}{\cosh(\ln\tau/\tau_{CC})+\sin\beta\pi}$
Cole/Davidson	$\frac{1}{(1+i\omega\tau_{CD})^\gamma}$ $0<\gamma\le 1$	$\cos(\Phi)^\gamma\ \cos\gamma\Phi$ $\tan\ \Phi=\omega\tau_{CD}$	$\cos(\Phi)^\gamma\ \sin\gamma\Phi$ $\tan\ \Phi=\omega\tau_{CD}$	$\frac{\sin\gamma\pi}{\pi}\left[\frac{\tau}{\tau_{CD}-\tau}\right]^\gamma$ for $\tau\le\tau_{CD}$ 0 for $\tau>\tau_{CD}$
Havriliak/Negami	$\frac{1}{(1+(i\omega\tau_{HN})^\beta)^\gamma}$ $0<\beta\le 1$ $0<\beta\gamma\le 1$	$r(\omega)\cos\,[\gamma\psi(\omega)]$ $r(\omega)=\left[1+2(\omega\tau_{HN})^\beta\cos\left(\frac{\beta\pi}{2}\right)+(\omega\tau_{HN})^{2\beta}\right]^{-\gamma/2}$ $\psi(\omega)=\arctan\left[\frac{\sin(\beta\pi/2)}{(\omega\tau_{HN})^{-\beta}+\cos(\beta\pi/2)}\right]$	$r(\omega)\sin\,[\gamma\psi(\omega)]$	$\frac{1}{\pi}y^{\beta\gamma}(\sin(\gamma\Theta(y))\Omega(y)$ $y=\tau/\tau_{HN}$ $\Omega(y)=[1+2y^\beta\cos(\pi\beta)+y^{2\beta}]^{-\gamma/2}$ $\Theta(y)=\arctan\left[\frac{\sin(\pi\beta)}{y^\beta+\cos(\pi\beta)}\right]$

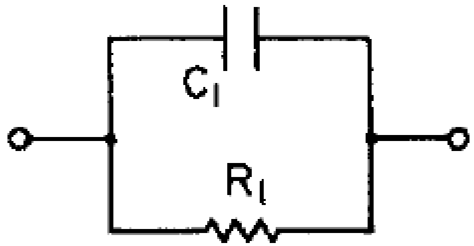
Electrical properties

Measurements: parallel plane capacitor



Up to ~3MHz

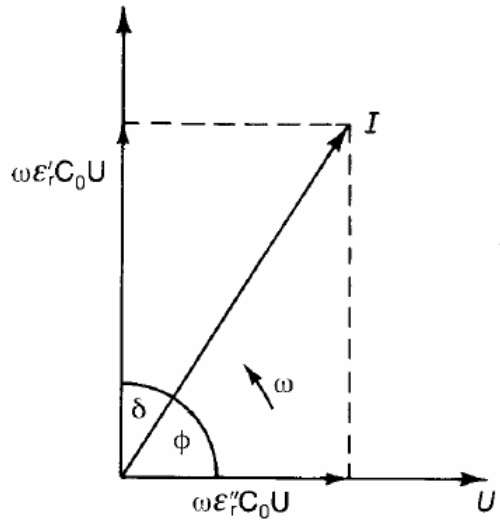




$$\varepsilon' = \frac{C\,d}{A}$$

Conductive samples (σ) $\tan\delta = \dfrac{\sigma}{\omega\varepsilon'}$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$



Capacitative and 'loss' components of total current I.

- Need for EMI shielding
- Coaxial cables
- Rest of setup similar to the resistivity

Dielectric properties laboratory